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Patentanwälte

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Re.: **International Patent Application PCT/EP2004/008397**
De Nora Elettrodi S.p.A.

Further to the written opinion of the International Search Authority dated
November 09, 2004:

Enclosed herewith are new claims 1-25 which should form the basis for further examination.

New claim 1, directed to method for the manufacturing of an electrode, is derived from claims 19 and 1 as originally filed. New claims 2 to 12 are derived from claims 2 to 8, claims 9, 12, 20 and 21 as originally filed.

New claim 13, directed to an anode, has been appended to claim 1 and the claims dependent therefrom. New claims 14 and 15 correspond to claims 13 and 14 as originally filed.

New claim 16, directed to precursor solution, is based on claims 1, 3 and the passage at page 4 lines 1 to 6 of the description. Claims 17 to 21 correspond to claims 4 to 8 as originally filed.

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New claims 22 to 25 correspond to claims 15 to 18 as originally filed.

Claim 1

Novelty and inventive step have been acknowledged for claim 19 as originally filed. Indeed, neither of the references D2, D3 or D4 anticipates or reasonably suggests the claimed method.

D2 discloses a method for the formation of a tin-containing coating on a valve metal using stannous octoate (see D2, page 4 lines 54 to 57). As discussed at page 3 lines 2 to 10 of the present application, the use of tin organic salts presents drawbacks, the most evident of which consists in the use of solvents which is disadvantageous in terms of costs of treatment and disposal of organic solvents. Moreover, tin organic salts are very sensible to moisture, and give easily rise to scarcely coherent and compact oxide layers. Finally, said organic precursors may provoke, during the pyrolysis step, the partial reduction of the coexisting noble metal oxide, with negative consequences in terms of chemical stability and catalytic activity.

D3 discloses a method for the preparation of an electrode comprising physical vapor deposition of a mixture comprising ruthenium oxide and at least one non-noble metal oxide, e.g. tin oxide.

D4 discloses an electrode having provided thereon an intermediate layer that is formed by tin-plating. The tin-plating is oxidised to convert the tin partly to tin oxide (see D4, claim 8).

The chemical nature of the precursor as used in the present invention can be assimilated to the one of HCl peptised-stannic acids. The thermal decomposition of β -stannic acids is characterised by an initial loss of water absorbed by physical bonds followed by the progressive release of hydrogen bridge-bonded chemisorbed water. The SnO_2 coating maintains a significant degree of hydroxylation even at temperatures above 400°C , which indicates a particular thermal stability of the surface -OH groups, which have ion-exchange properties and are responsible for many of the electrocatalytic features of SnO_2 coatings. The inventors have found that the preparation of tin dioxide coatings starting from hydroxychlorides leads to particularly high tin deposition yields, moreover, the properties of stability, electrocatalytic activity and reproducibility of coatings obtained from hydroxychlorides are very high.

Claim 13

It is clear from the above discussion, that an anode prepared by the method of claim 1 is substantially different from the electrodes known from D2, D3 or D4. Accordingly, the subject matter of claim 13 has to be considered novel and inventive.

Claim 16

This claim has been restricted to non-stoichiometric stannic hydroxychlorides or hydroxychlorides wherein the chloride anion has been partially replaced by an organic group. Novelty and inventive step have already been acknowledged for these precursor solutions.

Claim 22

Applicant disagrees with the finding that the subject of this claim is anticipated by D1. D1 discloses preparation of oxalostannic acid by oxidising freshly prepared stannous oxalate with H_2O_2 in an aqueous medium. It is submitted that the title of the Derwent abstract (making reference to *oxidising stannous chloride with hydrogen peroxide in water*) does not adequately reflect the teaching of D1 and is incorrect. Accordingly, D1 cannot destroy the novelty of claim 22.



(Wolfgang Thalhammer)

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Encl.
New claims 1 to 25

CLAIMS: IAP20 Res 05 JAN 2006

1. A method for the manufacturing of an electrode, comprising the application of a solution of a precursor for the pyrolytic formation of a tin-containing coating to a substrate of a valve metal, followed by the execution of thermal treatment, wherein the precursor solution comprises stannic hydroxychloride.
2. The method of claim 1 wherein said stannic hydroxychloride is a non-stoichiometric compound expressed by the formula $\text{Sn}(\text{OH})_{2+x}\text{Cl}_{2-x} \cdot n\text{H}_2\text{O}$, wherein the Cl:Sn molar ratio is comprised between 1 and 1.9.
3. The method of claim 1 wherein said stannic hydroxychloride is a compound expressed by the formula $\text{SnO}(\text{H}_2\text{O})_n\text{R}_{2-x}\text{Cl}_x$, R being an organic substituent.
4. The method of claim 3 wherein the Cl:Sn molar ratio is comprised between 1 and 1.9.
5. The method of claim 3 or 4 wherein R is the acetic group ($\text{CH}_3\text{COO}-$).
6. The method of any one of the previous claims further comprising a precursor of at least one noble metal.
7. The method of claim 6 wherein said precursor of at least one noble metal is a chlorinated precursor of iridium or ruthenium.
8. The method of claim 7 wherein said chlorinated precursor of iridium is H_2IrCl_6 .
9. The method of anyone of claims 1 to 8 wherein a valve metal is titanium or titanium alloy optionally provided with a ceramic pre-layer.
10. The method of claim 9 wherein the ceramic pre-layer comprises titanium dioxide.

11. The method of anyone of claims 1 to 10 wherein said application of the solution is effected in multiple coats, each followed by a thermal treatment.
12. The method of anyone of claims 1 to 11 wherein said thermal treatment is a pyrolysis at a temperature comprised between 350 and 800°C, optionally preceded by a drying at a temperature comprised between 80 and 200°C.
13. An anode provided with an electrocatalytic coating comprising tin, preferably tetravalent and in form of mixed oxide, prepared by the method of any one of the previous claims.
14. The anode of claim 13, prepared by the method of claim 6, wherein said coating has electrocatalytic properties toward the chlorine evolution reaction and said at least one noble metal is ruthenium.
15. The anode of claim 13, prepared by the method of claim 6, wherein said coating has electrocatalytic properties toward the oxygen evolution reaction and said at least one noble metal is iridium.
16. A solution of a precursor for the pyrolytic formation of a tin-containing coating, comprising a stannic hydroxychloride species selected from a non-stoichiometric compound expressed by the formula $\text{Sn}(\text{OH})_{2+x}\text{Cl}_{2-x} \cdot n\text{H}_2\text{O}$ and a compound expressed by the formula $\text{SnO}(\text{H}_2\text{O})_n \text{R}_{2-x}\text{Cl}_x$, wherein R is an organic substituent.
17. The solution of claim 16 wherein the Cl:Sn molar ratio is comprised between 1 and 1.9.
18. The solution of claim 16 or 17 wherein R is the acetic group.
19. The solution of any one of claim 16 to 18 further comprising a precursor of at least one noble metal.

20. The solution of claim 19 wherein said precursor of at least one noble metal is a chlorinated pre-cursor of iridium or ruthenium.
21. The solution of claim 20 wherein said chlorinated precursor of iridium is H_2IrCl_6 .
22. A method for the manufacturing of a precursor solution for the pyrolytic formation of a tin-containing coating comprising the addition of hydrogen peroxide to a stannous chloride solution, optionally under temperature and redox potential control.
23. The method of claim 22 wherein the Cl:Sn ratio in the solution is decreased by subsequent reduction of metallic tin and further addition of hydrogen peroxide, optionally under temperature and redox potential control.
24. The method of claim 22 or 23 wherein said stannous chloride solution further contains a precursor of an organic substituent.
25. The method of claim 24 wherein said precursor of an organic substituent is acetic acid.

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